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MUON SPIN DEPOLARIZATION IN NONMAGNETIC METALS DOPED WITH PARAMAGNETIC IMPURITIES

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I. INTRODUCTION

One of the most active fields of study using the technique of muon spin rotation (μSR) is the diffusion of light interstitial particles in a metallic host lattice. A comparison of muon diffusion with the diffusion of the heavier hydrogen isotopes offers the possibility to study different mechanisms of particle motion; the light mass of the muon, for instance, may allow a coherent or band-like motion which is negligible for the heavier particles. In order for such studies to be particularly fruitful, however, a wide range of host metals must be examined.

Information on muon diffusion is derived from the temperature dependence of the muon depolarization rate, which in the case of transverse field μSR measurements in non-magnetic metals, is produced by the inhomogeneous magnetic field distributions of the host nuclear dipole moments. Consequently, there are two limitations inherent in such studies: (a) as the muon motion becomes too rapid the field inhomogeneities are averaged to zero and no depolarization is produced and (b) many host materials have negligible nuclear moments. In the first case, an upper limit to the muon diffusion rate is reached at low temperatures; in copper no depolarization is observed at temperatures greater than about 240 K[1]. This restricts the comparison with hydrogen diffusion which is measured at much higher temperatures. In the latter case, no information on muon diffusion can be obtained at all, as in for example silver or gold.

A second very interesting field of investigation in solid state physics using the μSR technique is the behavior of magnetic materials. In studying magnetism with muons, it is first necessary to understand the nature of the interaction between the muon and the magnetic ions; only then can μSR become a reliable tool to study the intrinsic magnetic behavior of the host material. In addition, because the muon is such a simple magnetic probe (i.e., a bare dipole in free space), its interaction with magnetic ions is a problem of interest in itself since such interactions should be well understood if current theories of magnetism in solids are well-founded.

In the ensuing discussion we treat both the subjects of the diffusion of muons and their magnetic interactions by describing the physics to be learned from experiments which measure μ^+ depolarization in metallic hosts doped with dilute concentrations of magnetic impurities. In studying diffusion, such systems provide a depolarization mechanism even in the absence of host nuclear moments. Furthermore, the larger ionic dipole moment (with respect to nuclei) means that larger diffusion rates can be measured. A complete treatment of such experiments requires an understanding of the nature of the magnetic coupling between the muon and the impurity ion, however. Furthermore, one must take into account the ion spin relaxation time which is several orders of magnitude shorter than that of the host nuclei and is thus comparable to the correlation time associated with the muon motion. Thus, three quantities are of physical interest in these experiments: the muon diffusion rate D_μ, the ion spin relaxation time τ_s, and the nature and strength of the interaction G between the muon and the magnetic ion.

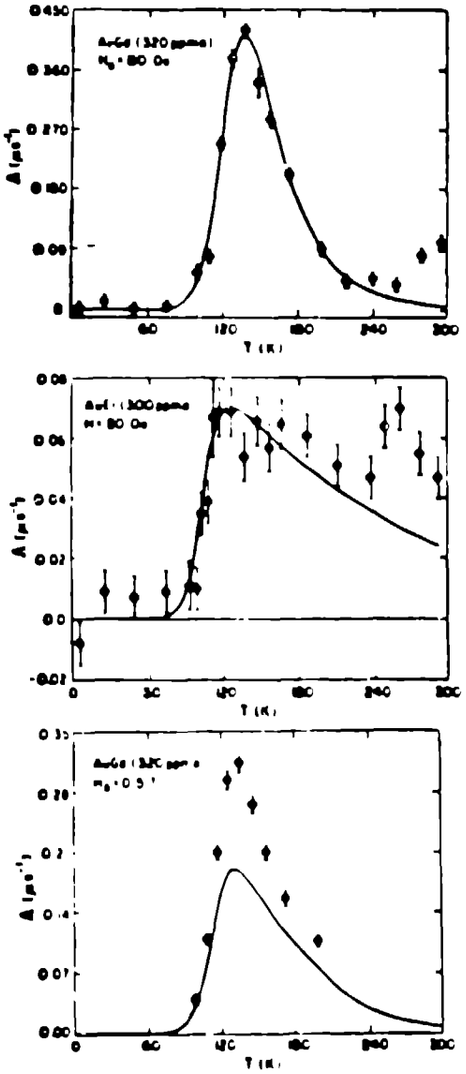

Fig. 1

Temperature dependence of the depolarization rate for AuGd (a), AuEr (b) at 80 Oe applied field and for AuGd at 5 kOe (c). The solid lines in (a) and (b) are fits to the data. The parameters are given in Table I. The solid line in (c) is the high field dipolar prediction using the same parameters.

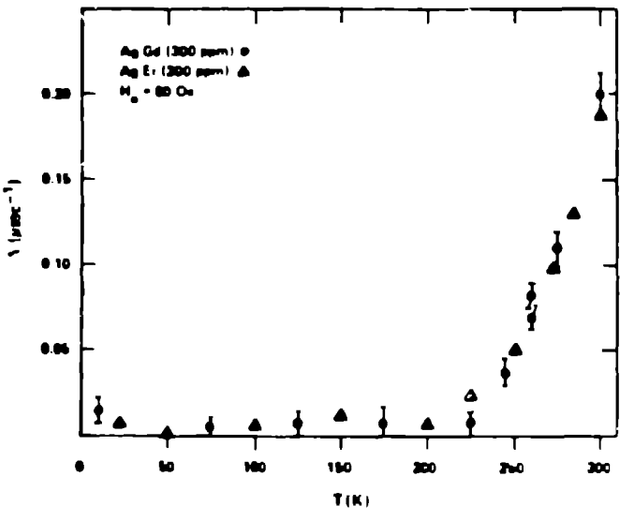

Fig. 2

Temperature dependence of the depolarization rate at 80 Oe for AgGd and AgEr.

II. DESCRIPTION OF EXPERIMENTS

The experiments described here were carried out at the Stopped Muon Channel of LAMPF by a team of scientists from Los Alamos, Rice University, Sandia Laboratories in Albuquerque and Ames Laboratories. Samples of the noble metals Cu, Ag, and Au were doped with the rare earths Gd and Er and with the transition element Mn. The concentrations studied were all below 500 ppm at. The samples were prepared by arc melting and were annealed at 800° C for one hour in an inert atmosphere. Resistivity measurements were consistent with a homogeneous, random distribution of impurity ions and were used to verify the concentrations of magnetic impurities.

The systems under study were chosen for their high solubilities (to ensure a random distribution of ions) and because the ion spin dynamics have been well-studied by ESR at low temperatures. Furthermore, the host metals have quite different Debye temperatures and thus may be expected to exhibit different diffusion rates for muons. In addition, the muon diffusion rate in Cu is known for 70 K < T < 240 K; Au and Ag have small nuclear moments and so diffusion is not measurable in the pure hosts. Gd and Er were chosen as examples of an S-state ion (Gd)

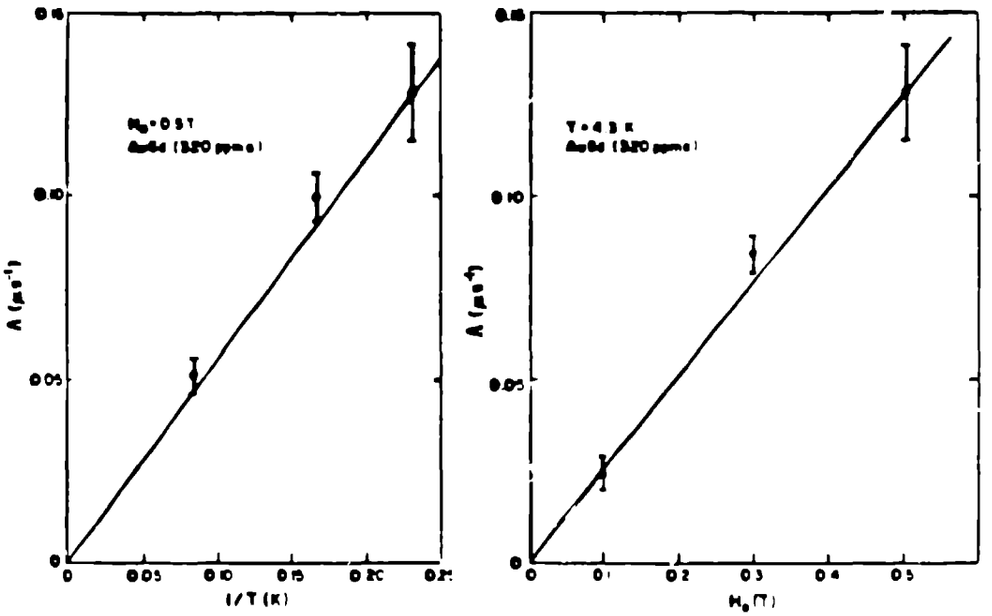

Fig. 3

Temperature and field dependence of the depolarization rate for AuGd at low temperatures and high fields. The solid line is calculated from Ref. 2.

and a cyrstal-field split ion (Er). The rare earths are nearly insoluble in Cu and so the S-state ion Mn was chosen as a solute.

Figure 1 shows data taken in Au hosts doped with about 300 ppm at. Er and Gd. Since the depolarization rate $\Lambda(T)$ was found to be negligible in the pure host, all of the structure observed is due to interactions with the magnetic ions. The solid lines are fits to the data as discussed below. The data in Figs. 1a and 1b were taken at 80 Oe. The data for AuGd in Figure 1c was taken at about 5 kOe and show about a 25% decrease in Λ (at the peak) from the low field data. Not shown in Fig. 1 are measurements made with rare earth concentrations of 100 ppm at. It was found at all temperatures that the depolarization rate was decreased by a factor of 3(± 5%) from the 300 ppm at. data, reflecting a linear concentration dependence. Figure 2 shows measurements made at 80 Oe on Ag samples doped with about 300 ppm at. concentrations of Er and Gd. In Fig. 3 the depolarization rate for AuGd taken at low temperatures and high fields are shown. Finally, values for the depolarization rate measured in CuMn (500 ppm at.) between 50 K and 300 K were found to be identical to those obtained in the pure Cu host. From the known μ^+ diffusion rate in Cu[1], one may deduce that the muons move too slowly to diffuse to the vicinity of the Mn ions at these temperatures.

III. MODEL FITS TO THE Au HOST DATA

A. $T < 6$ K; 1000 Oe $< H <$ 5000 Oe

The data shown in Fig. 3 for AuGd show that for $T \leq 6$ K and $H \leq 5000$ Oe, the depolarization rate is proportional to H/T. Furthermore, the line shape is found to be Lorenztian. This is precisely the behavior one expects for a motionless muon whose line shape is inhomogeneously broadened by a spatially random distribution of slightly polarized magnetic ions. The expected magnitude of the depolarization rate for such a case can be calculated[2] assuming both a dipolar interaction and an ion relaxation time $\tau_s \ll 2\pi/\omega_\mu$, where ω_μ is the muon Larmor precession frequency. For 320 ppm at. Gd in Au, one obtains

$$T_2^{-1} = 1.08 \times 10^{-4}\ H/T\ \mu sec^{-1},$$

a plot of which is shown as the solid line in Fig. 3. As discussed below, the broadening due to the RKKY interaction[3] is found to be about ten times smaller. We therefore conclude from the excellent agreement with these data that the long range part of the muon-ion interaction is dipolar, and that both the muons and the ions are stationary and are randomly distributed in the lattice.

B. $T > 50$ K; $H = 80$ Oe

Any mathematical model used to fit the data must incorporate both the muon and ion dynamics as well as correctly account for the interaction mechanism. A similar situation arises in NMR studies of superionic conductors doped with paramagnetic impurities[4]. The model used here is due to P. M. Richards[5] which is a generalization of earlier calculations. The general assumptions of Richards' model are that (a) the muon motion is described by a classical diffusion equation with no trapping, (b) the interaction is isotropic and varies spatially as $1/r^6$ with a cutoff at a distance of closest approach, (c) there is no correlation in ionic states between one muon hop and the next, and (d) there is no inhomogeneous broadening. In addition to these general features of the model, it is further assumed in the fits described below that (e) the interaction is a classical dipolar one, that (f) the ion relaxation time τ_s varies as β/T, and that (g) the muon diffusion coefficient D_μ is given by $D_\mu = D_0 \exp(-\varepsilon/T)$. Classically, the hopping time τ_h is then $\tau_h = d^2/6D_\mu$, d being the distance for a single hop. Fits were carried out for a distance of closest approach corresponding to the tetrahedral and octahedral interstitial sites. In addition, it was necessary to introduce an arbitrary parameter α to renormalize the interaction strength. The results of these fits for the AuGd and AuEr data using the tetrahedral site are shown as solid lines in Fig. I; the parameters are given in Table I.

Before discussing the physical significance of the fit parameters, it is instructive to qualitatively discuss the behavior of the data within the context of the model calculations. At the very lowest temperatures no μ^+ depolarization is observed since the muons are essentially stationary and the ions are not polarized significantly at 80 Oe. As the temperature is increased, the muons move more rapidly and eventually diffuse close to the ions producing a measurable depolarization. In this diffusion limited regime, a single encounter with an ion produces large dephasing of the muon spin and T_2 is characterized by the time to diffuse to a given ion, τ_h. The peak occurs very roughly at the temperature where $(\alpha G\tau) = 1$, where αG characterizes the interaction amplitude and τ is now an effective correlation time which has been taken to be $1/\tau = 1/\tau_s + 1/\tau_h$. At higher temperatures (beyond the first peak) the muon encounters many ions in its lifetime, each encounter producing a small amount of dephasing. In this regime, T_2 is characterized by the effective correlation time τ at the ion site. Finally, at all temperatures, one expects the depolarization rate to vary

We now discuss these fits quantitatively, pointing out that no attempt has yet been made to fit the double peak structure. In the case of AuGd the value of β was fixed at 7 nsec -K by the results of low temperature ESR measurement[6]. The extrapolation of the ESR Korringa relaxation rate[7] to higher temperatures for Gd appears reasonable since the orbital angular momentum vanishes to lowest order and hence phonon-induced relaxation should be small. The rate of rise of the depolarization rate at lower temperatures and the position and magnitude of the peak fix D_μ. On the high side of the peak at T > 140 K, $\Lambda(T)$ falls exponentially indicating that $\tau_h \ll \tau_s$. In order to fit the peak position and height an interaction strength of about 4-5 times dipolar is required.

For AuEr the depolarization rate on the low temperature side of the first peak is fit well by the diffusion rate obtained from the AuGd fits. On the high temperature side of the peak the depolarization rate fails as 1/T, indicating that $\tau_s \ll \tau_h$. A quantitative fit requires a knowledge of both the spin and effective g-factor for Er in Au. The ground state is a doublet with g = 6.8 and is split from the first excited state by about 16 degrees; the overall splitting due to the crystal fields is about 100 K[8]. Consequently, we have assumed for simplicity that all magnetic sublevels are populated at the temperatures of interest and have thus used S = 7.5 ħ and g = 1.2, the Landé value. In the fits to the data τ_s is highly correlated with the interaction strength. It was found that an interaction strength about 10-20 times dipolar is required to fit the peak position and height and that $\tau_s(\mathrm{Er})$ is about 100 times smaller than $\tau_s(\mathrm{Gd})$.

C. T > 50 K; H = 5000 Oe

Figure 1c shows the depolarization rate for AuGd at H = 5024 Oe for 100 K < T < 200 K. The magnitude of the depolarization rate at the peak position is decreased by about 25% from its value at 80 Oe. A decrease in magnitude at field values where one has $\omega_s\tau \sim 1$ is predicted by both the dipolar and RKKY interaction models (ω_s is the ion Larmor precession frequency). For example, the homogeneous widths for a stationary muon are given by[9]

$$T_2^{-1} = G_D^2\,\tau\left[4 + \frac{13}{1+\omega_s^2\tau^2} + \frac{3}{1+\omega_\mu^2\tau^2}\right] \qquad \text{dipole}$$

$$T_2^{-1} = G_R^2\,\tau\left[1 + \frac{1}{1+\omega_s^2\tau^2}\right] \qquad \text{asymptotic RKKY}$$

where G_D and G_R contain the interaction strengths. The terms containing $\omega_s\tau$ and $\omega_\mu\tau$ arise from spin-flip terms in the interaction Hamiltonian. The solid curve in Fig. 1c is the 5000 Oe prediction for the dipolar interaction using the parameters obtained from the low field data. One sees that the agreement is not particularly good. As described below, one expects $G_R \ll G_D$, and thus high field data are not well-explained by either of these long-range interactions.

IV. DISCUSSION OF RESULTS

We now discuss the three physical quantities of interest derived from these experiments: the muon-ion interaction strength, the muon diffusion rate, and the ion spin relaxation times.

A. Interaction Strengths

Three distinct interaction mechanisms are most likely in the systems considered here: dipolar, RKKY, and contact or transferred hyperfine. The dipolar interaction can be calculated exactly and agrees well with the long range part of the interaction measured at low temperatures. The RKKY strength in the asymptotic limit[10] may be estimated if one knows the S-wave conduction electron coupling to both the 4f rare earth orbitals (J) and the muon (A). Using the low

Knight shifts[12], we find that $G_D \approx 10\, G_R$, and hence that the asymptotic RKKY interaction is unimportant.

A third mechanism for muon depolarization is an interaction which is mediated by the conduction electrons but which is short range in nature. The short range part of the RKKY interaction involving S-wave conduction electrons is such a possibility. Equally likely, however, is that such an interaction would be mediated by electrons having a 5d-like character. In AuGd the gadolinium is trivalent whereas the gold is monovalent; therefore, there is considerable charge screening of the gadolinium and some of the screening electrons have 5d character. Evidence for significant 4f-5d coupling in the rare earths has been found in dilute metal alloys[8,13,14] and in intermetallic compounds[15]. The interesting questions for muon studies involve the degree of overlap of the 5d wave functions at the muon site and the field dependence which such an interaction might produce. A model calculation similar to the one described here indicate that a contact field of about 35-40 kOe would be required[18].

Before drawing conclusions regarding the nature of the ion-muon interaction, it is important to consider the model dependence of the interaction strengths obtained from fitting the data, focussing on the apparent weakness of the dipolar interaction. Two parameters in the model are strongly correlated with the interaction strength, namely, the distance of closest approach a_o and τ_s. We have taken a_o to be that corresponding to a normal interstitial site. Because of the assumed $1/r^6$ spatial variation, small changes in a_o affect the calculated depolarization rate considerably; consequently, it could be that the muon-ion pair sufficiently deform the lattice so that a_o is smaller than expected for a tetrahedral or octahedral site, thus increasing the effective interaction strength. This picture alone, however, will not reconcile the differences between Er and Gd in Au since the ionic radii for Er and Gd differ only by about 5% and thus any deformations should be about the same.

It is also possible that the presence of the muon changes the electron spin density at the ion site and thus also changes τ_s from its ambient value. Calculations[16] of the spin density enhancement produced nearby the muon in undoped metal indicate a change of only few percent, however. Thus although this could be a factor, it is not expected to be a large one. The possibility that the muons electric field gradient affects τ_s significantly and hence the fit for the interaction strength also cannot be excluded, though it seems unlikely.

In addition to these considerations, the model for muon diffusion used here may have important inadequacies which could account for at least some of the apparent reduction in dipolar strength. For example, the model specifically excludes muon trapping. If trapping is present, however, it must be weak since the precisely linear concentration dependence which is measured precludes saturation of any supposed traps. Furthermore, impurity induced muon trapping in other FCC and BCC metals has been found to be mostly negligible above 100 K[17]. Thus the assumption of no trapping appears to be reasonable.

A more serious objection may involve the use of the continuum approximation which is inherent in treating the muon motion with a classical diffusion equation. Because the dipole interaction falls off so sharply with distance, the discrete nature of the hopping in a lattice can be important and can lead to a larger depolarization rate for a given interaction strength than is obtained from a continuum of distances. Indeed, calculations[18] which mock up muon-hopping on a real lattice show just such an effect. It is unlikely, however, that the differences between Gd and Er can be resolved by such a mechanism.

We conclude therefore that neither the dipolar nor asymptotic RKKY type interactions can account for all of the interaction strength observed. This conclusion is based upon the small value for the calculated asymptotic RKKY interaction and the inadequacy of the dipolar interaction to explain the

coupling in AuGd at 80 Oe, the differences in coupling between AuGd and AuEr and the high field-high temperature AuGd results. Consequently, the possibility of a short range interaction as, for example, one mediated by 5d virtual bound state electrons, deserves serious consideration.

B. Diffusion Rates

Before discussing the value of the muon diffusion rate in Au, several points need to be made. Although the precise nature of the interaction is not known for μ^+ in AuGd, the strength has been determined (~ 4-5x dipolar) and hence D_μ is reasonably well-known within, of course, the context of the model used. Furthermore, the possibility that the muon diffusion is influenced by long-range strains induced in the lattice by the substitutional impurities seems remote. The solubilities are high and hence the lattice deformations should be confined to the sites nearest the impurity ions.

The diffusion rate for muons below room temperature in Cu has been derived from measurements[1] in the pure host and is given in Table I along with the measurements for Au. From the magnitudes of the pre-exponential factors and activation energies for the diffusion coefficients, one may conclude that the diffusion mechanisms for muons in Cu and Au are very different; indeed, muons in Au resemble somewhat hydrogen in Cu. The large pre-exponential factor suggests that muons are undergoing over-the-barrier hopping in Au, whereas in Cu significant incoherent tunneling is involved. (See ref. 19 for a discussion of muon and hydrogen diffusion in Cu.)

Although the lack of data for μ^+ above room temperature precludes a determination of D_μ in Ag, it is apparent by observation that $D_\mu(Au) > D_\mu(Ag) > D_\mu(Cu)$. This correlates qualitatively with simple models[20] of phonon-assisted diffusion which predict an increasing diffusion rate for a decreasing Debye temperature ω_D; indeed $\omega_D(Au) < \omega_D(Ag) < \omega_D(Cu)$.

C. Ion Spin Relaxation Times

The types of measurements described here offer the possibility of studying ion relaxation times in a temperature region where the ESR signals have become too broad to be detected. As discussed above, one requires a situation where $\tau_s < \tau_h$. The principal limitation to such studies, which may be formidable, is an accurate knowledge of the interaction strength between the muon and the ion.

The experiments on AuGd and AuEr have yielded $\tau_s(Er) << \tau_s(Gd)$ as might be expected. The measured $1/T$ dependence for $\tau_s(Er)$ is in principal consistent with relaxation via the conduction electrons (Korringa) or via direct phonon processes[21]. In the temperature range studied here, it is likely that the phonon processes will dominate, although a confirming calculation of the expected rates is difficult in a crystal field split system at temperatures which are neither very high nor very low compared to the overall splitting of about 100° K.

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TABLE I

Parameter	AuGd(a)	AuEr(a)	AuGd(b)	AuEr(b)	Cu
α	4.8 ± 0.1	17-12	4.1 ± 0.1	10	
β(nsec K)	7.0	0.05 - 0.10	7.0	0.1	
D_0(cm^2/sec)	0.044 ± 0.008		0.013 ± 0.003		1.73×10^{-9}
ε(K)	1631 ± 25		1482 ± 25		560

Parameters obtained assuming the muon hops on octahedral (a) and tetrahedral sites (b). The same diffusion parameters, D_0 and ε, were used for both AuGd and AuEr. For AuEr a range of possible values for the interaction strength enhancement α and for relaxation time β are shown for octahedral sites; a similar range exists for the tetrahedral case. The Cu values are from reference 1.

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